Indian Journal of Chemistry
Vol. 14A, February 1976, pp. 97-99

Force Constant, IR Absorption Frequency & Debye Temperature of Li, Na, K, Rb, Cs, Ag(I), Tl(I) & Cu(I) Halide Crystals

K. P. THAKUR*
Department of Physics, S.P. College, Dumka 814101
and
L. THAKUR
P.G. Department of Chemistry, Bhagalpur University, Bhagalpur 812007

Received 10 *December* 1974; *accepted* 8 *April* 1975

The expressions for the force constant (f), IR absorption frequency (ν_0) and Debye temperature (θ_D) of Li, Na, K, Rb, Cs, Ag, Tl and Cu halide crystals have been obtained on the basis of Gaussian and the modified Gaussian interatomic potential functions employing the approach which involves the use of molecular force constant and internuclear distance for evaluating the potential parameters. The potential parameters used in the calculations have been obtained by a method which utilizes the molecular constants known to a high degree of accuracy. The plot of Debye temperature of the alkali halides, obtained from the modified Gaussian function, against their reduced mass shows that the halides of an alkali metal fall on a linear plot. This regularity is most pronounced for Li, Na, K and Cs halides where the points are mostly on the linear plot, while for Rb halides it is less pronounced.

SEVERAL attempts have been made to compute the values of the force constant, IR absorption frequency and Debye temperature of the ionic crystals on the basis of different forms of potential functions[1-11]. In the conventional procedure[12], compressibility data at 0°K are used to evaluate the constants of potential energy functions, but this involves much error and moreover the experimental compressibility values are not always known.

The aim of the present work is to evaluate the values of the force constant, IR absorption frequency and Debye temperature of alkali halide and heavy metal halide crystals, from Gaussian and modified Gaussian potential functions in which we have used a different approach[13] involving the use of molecular force constant and internuclear distance for evaluating the potential parameters.

Theoretical

The potential energy, $\phi(r)$, of a pair of unlike ions in an ionic crystal, can be represented mainly in terms of the coulombic attractive term, $-Me^2/r$, and the non-coulombic term, $\Psi(r)$. Thus,

$$\phi(r) = -Me^2/r + \Psi(r) \qquad ...(1)$$

where M is the Madelung constant, e the electronic charge, and r the interionic distance.

According to the Gaussian potential due to Varshni and Shukla[14] and the modified Gaussian potential due to Patel *et al.*[15] the non-coulombic repulsive term in an ionic crystal may be expressed as

$$\Psi(r) = P \exp(-pr^2) \text{ (Gaussian)} \qquad ...(2)$$

$$\Psi(r) = Q \exp(-qr^{3/2}) \text{ (modified Gaussian)} \qquad ...(3)$$

where P, p, Q and q are potential parameters.

*To whom all correspondence should be addressed.

The potential parameters p and q have been evaluated using the molecular stability and force constant conditions[13] (4) and (5) respectively.

$$U'(r_e) = 0 \qquad ...(4)$$

$$U''(r_e) = k_e \qquad ...(5)$$

where r_e is the equilibrium interionic distance of the gaseous molecule and $U'(r)$ and $U''(r)$ refer to the first and second derivatives of $U(r)$ which is the potential energy of an unlike ion pair in the gaseous state.

Application of conditions (4) and (5) to the Gaussian potential and modified Gaussian potential yields expressions (6) and (7) for the potential parameters p and q respectively.

$$p = \frac{1}{2r_e^2}\left[\frac{k_e r_e^3}{e^2} + 3\right] \qquad ...(6)$$

$$q = \frac{2}{3r_e^{3/2}}\left[\frac{k_e r_e^3}{e^2} + \frac{5}{2}\right] \qquad ...(7)$$

Application of the crystal stability condition[12] to the Gaussian potential and modified Gaussian potential yields expressions (8) and (9) for the potential parameters P and Q respectively.

$$P = \frac{Me^2 \exp(pr_0^2)}{2pr_0^3} \qquad ...(8)$$

$$Q = \frac{2Me^2 \exp(qr_0^{3/2})}{3qr_0^{5/2}} \qquad ...(9)$$

where r_0 is the equilibrium interionic distance in the crystalline state.

According to Krishanan and Roy[3], the force constant (f) is given by Eq. (10).

$$f = \frac{1}{3}\left[\Psi''(r_0) + \frac{2}{r_0}\Psi'(r_0)\right] \qquad ...(10)$$

where $\Psi'(r)$ and $\Psi''(r)$ refer to the first and second derivatives of $\Psi(r)$.

Condition (10) when applied to Eqs. (2) and (3) yields expressions (11) and (12) for the force constansts derived from the Gaussian and modified Gaussian potential functions respectively.

$$f = \frac{2}{3}Pp \exp(-pr_0^2)(2pr_0^2-3) \quad ...(11)$$

$$f = \frac{Qq}{4r_0^{1/2}}(3qr_0^{3/2}-5) \exp(-qr_0^{3/2}) \quad ...(12)$$

The IR absorption frequency is related to the force constant by relation (13).

$$\nu_0 = \frac{(f/m)^{1/2}}{2\pi} \quad ...(13)$$

where m is the reduced mass.

From Eqs. (11), (12) and (13), we get expressions (14) and (15) for the IR absorption frequencies according to the Gaussian and modified Gaussian potential energy functions respectively.

$$\nu_0 = \left[\frac{2Pp(2pr_0^2-3) \exp(-pr_0^2)}{12m\pi^2}\right]^{1/2} \quad ...(14)$$

$$\nu_0 = \left[\frac{Qq(3qr_0^{3/2}-5) \exp(-qr_0^{3/2})}{16m\pi^2 r_0^{1/2}}\right]^{1/2} \quad ...(15)$$

Once the value of ν_0 is known, Debye temperature (θ_D) can be computed from relation (16).

$$\theta_D = \frac{h\nu_0}{k} \quad ...(16)$$

where h is Planck's constant and k the Boltzmann constant.

Results and Discussion

In the present calculation, the values of r_e, k_e and r_0 given in Table 1 were taken from various sources[13,16,17], where the original sources are given. The values of f, ν_0 and θ_D calculated according to the Gaussian and modified Gaussian potential energy functions are given in Table 2 along with the available experimental values[6-10,18,19]. The force constant values are sensitive to the type of potential energy functions used. The largest and smallest values of the force constant were obtained for LiF and CsI respectively. These values are compatible with the observed bond length and bond energy measurements[16,17]. It can be seen from Table 2 that the values of ν_0 and θ_D derived from the modified Gaussian potential energy functions are closer to the experimental data than those obtained from the Gaussian function. The discrepancies between the observed and computed values of ν_0 and θ_D are explained by the fact that minor terms in the expression of the force constant have been neglected in the present study. The poor agreement in some cases shows the limitations of the potential energy functions used. From these calculations it can be inferred that the modified Gaussian function is better than the Gaussian function. The zero point energy (ϵ) can be computed from the Debye temperature data using relation (17).

$$\epsilon = 9k\theta_D/4 \quad ...(17)$$

TABLE 1 — EXPERIMENTAL VALUES OF THE PARAMETERS r_e, k_e AND r_0 USED IN THE CALCULATIONS

Crystal	r_e (Å)	r_0 (Å)	$k_e \times 10^{-5}$ (dyne/cm)
LiF	1·545	2·014	2·4586
LiCl	2·037	2·570	1·4982
LiBr	2·1704	2·751	1·2467
LiI	2·392	3·000	0·9719
NaF	2·007	2·307	1·465
NaCl	2·361	2·820	1·1004
NaBr	2·502	2·989	0·9582
NaI	2·711	3·237	0·7626
KF	2·171	2·674	1·2038
KCl	2·6677	3·147	0·8640
KBr	2·821	3·298	0·7009
KI	3·048	3·533	0·5264
RbF	2·265	2·815	0·3913
RbCl	2·787	3·291	0·7666
RbBr	2·945	3·445	0·6697
RbI	3·177	3·671	0·4924
CsF	2·345	3·004	1·4500
CsCl	2·906	3·571	0·7195
CsBr	3·072	3·720	0·5675
CsI	3·315	3·956	0·3897
AgCl	2·8808	2·772	1·8330
AgBr	2·3922	2·884	1·6785
TlCl	2·4848	3·33	1·4540
TlBr	2·6181	3·44	1·2603
TlI	2·8135	3·62	1·0380
CuCl	2·0500	2·34	2·2840
CuI	2·3340	2·62	1·7340

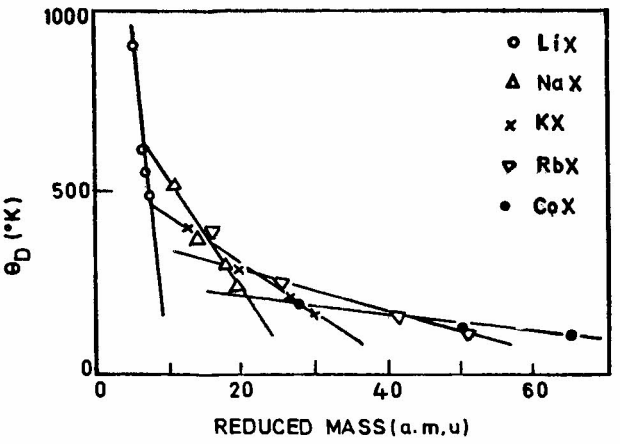

Fig. 1 — Plots of Debye temperature (θ_D) against the reduced mass of alkali halides

Since the IR absorption frequencies and hence the specific heat and the Debye temperature of a solid are dependent upon the relative masses of the vibrating ions, we have plotted the Debye temperature of the alkali halides, obtained from the modified Gaussian function, against their reduced mass (Fig. 1). The grouping has been done on the basis of alkali metal ion. It is observed that all the members of a group fall on a linear plot. This regularity is most pronounced for Li, Na, K and Cs

TABLE 2 — CALCULATED AND OBSERVED VALUES OF FORCE CONSTANT (f), IR ABSORPTION FREQUENCY (ν_0) AND DEBYE TEMPERATURE OF THE ALKALI HALIDE AND HEAVY METAL HALIDE CRYSTALS

Crystals	$f\times10^{-4}$ (dyne/cm)*		$\nu_0\times10^{-12}$ (sec^{-1})*			θ_D(°K)*		
	G	MG	G	MG	Expl	G	MG	Expl
LiF	15·0	11·6	20·8	18·7	9·2	999	896	732
LiCl	6·4	6·4	14·8	13·0	—	711	622	—
LiBr	6·9	5·8	12·8	11·8	—	616	564	—
LiI	5·4	4·5	11·2	10·3	—	535	492	—
NaF	11·7	7·5	13·1	10·5	7·4	629	503	—
NaCl	6·1	4·9	8·2	7·4	4·9	393	353	321
NaBr	5·3	4·7	6·7	6·3	4·0	323	303	—
NaI	4·2	3·7	5·8	5·4	3·5	276	258	1 95
KF	6·8	5·8	9·0	8·3	—	432	398	—
KCl	4·8	4·2	6·3	5·9	4·3	300	282	236
KBr	3·9	3·5	4·8	4·5	3·4	228	216	188
KI	2·9	2·4	3·9	3·5	2·9	185	169	163
RbF	7·5	6·3	8·6	7·9	—	412	376	—
RbCl	4·2	3·8	5·1	4·8	3·5	244	229	—
RbBr	3·7	3·3	3·7	3·5	2·6	177	167	—
RbI	2·8	2·5	2·9	2·7	2·3	138	130	118
CsF	7·5	4·8	8·3	6·6	—	399	319	—
CsCl	3·9	3·4	4·6	4·3	2·9	221	206	—
CsBr	3·1	2·7	3·1	2·9	2·5	148	138	—
CsI	2·2	2·3	2·3	2·3	—	109	111	—
AgCl	9·7	7·0	7·4	6·3	3·1	356	303	184
AgBr	8·9	7·8	5·4	5·1	2·4	260	245	144
TlCl	7·3	7·6	6·1	6·2	2·6	290	297	—
TlBr	6·4	5·4	4·1	3·8	1·9	197	181	—
TlI	4·6	4·5	3·0	3·0	—	144	142	—
CuCl	11·8	10·8	8·9	8·5	5·7	427	408	—
CuI	9·1	8·3	5·7	5·5	—	274	267	—

*G and MG refer respectively to the Gaussian and modified Gaussian potentials.

halides while for Rb halides it is less pronounced. It is found that as the halide ion becomes bulkier the effect of the reduced mass on the Debye temperature is more pronounced for the lighter alkali metal ions and less so for heavier ones especially Cs^+. Thus the absolute value of the slope of linear plots decreases as we pass from Li to Cs group. Fig. 1 can be used for estimating the Debye temperatures of alkali halides for which data are not available. Moreover, this regularity linear plot can immediately show the correctness of the data.

References

1. THAKUR, K. P., *J. inorg. nucl. Chem.*, **36** (1974), 2171.
2. THAKUR, K. P. & PANDEY, J. D., *J. inorg. nucl. Chem.*, **37** (1975), 645.
3. KRISHANAN, K. S. & ROY, S. K., *Proc. roy. Soc. London*, **207A** (1951), 447.
4. SRIVASTAVA, S. P., SHARMA, M. N. & MADAN, M. P., *J. phys. Soc. Japan*, **25** (1968), 212.
5. MITRA, S. S. & JOSSI, S. K., *Physica*, **26** (1960), 284.
6. SHARMA, M. N. & MADAN, M. P., *Indian J. Phys.*, **38** (1964), 305.
7. BARRON, T. H. K., BERG, W. T. & MORRISON, J. A., *Proc. roy. Soc. London*, **202A** (1957), 476.
8. *American institute of Physics handbook* (McGraw-Hill, New York), 1963.
9. REDDY, P. J., *Physica*, **29** (1963), 63.
10. BOTTGEE, G. L. & GEDDES, A. L., *J. chem. Phys.*, **56** (1972), 3735.
11. JOSSI, S. K. & MITRA, S. S., *Proc. roy. Soc. London*, LXXVI, **2** (1960), 295.
12. BORN, M. & HUANG, K., *Dynamical theory of crystal lattices* (Clarendon Press Ltd, Oxford), 1957.
13. KACHHAVA, C. M. & SAXENA, S. C., *Phil. Mag.*, **8** (1963), 1429.
14. VARSHNI, Y. P. & SHUKLA, R. C., *J. chem. Phys.*, **35** (1961), 582.
15. PATEL, M. M., GOHEL, V. B. & TRIVEDI, M. D., *Indian J. Phys.*, **41** (1967), 235.
16. PANDEY, J. D. & SAXENA, O. C., *J. chem. Soc.*, A (1969), 397.
17. PANDEY, J. D., *J. phys. Soc. Japan*, **26** (1969), 579.
18. HUGGINS, M. L., *J. chem. Phys.*, **5** (1937), 143.